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COMPLETE SPECIFICATION

Cyclopropane Carboxylic Acid Derivatives and their use as Insecticides

We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation, established by Statute, of P.O. Box 236, Kingsgate House, 66—74 Victoria Street, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

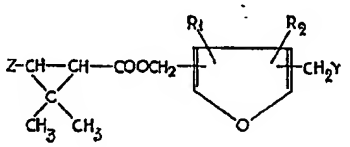
This invention relates to insecticidal derivatives of chrysanthemic and related acids, and to processes for their preparation.

The naturally occurring insecticide pyrethrum, obtained from the flower heads of *Chrysanthemum cinerariaefolium* and related species, is now a well established insecticide having a range of desirable biological properties, including a high insecticidal toxicity, and in its combination of favourable properties is superior to many synthetic insecticides which have become available. Unfortunately, however, natural pyrethrum is rather unstable in many formulations in common use and furthermore does not form a sufficiently persistent insecticidal film on all the materials and surfaces to which it is applied in practice. It is also expensive and must be imported from abroad.

Much has been done, therefore, to investigate synthetic insecticides in order to produce compounds having a combination of desirable biological and physical properties such as high toxicity to insects and very low mammalian toxicity, and this investigation has been facilitated by the determination of the structure of six related esters in natural pyrethrum. A number of esters of the so-called chrysanthemic and pyrethric acids and their derivatives have been prepared, notably allethrin, but even allethrin is inferior in many respects to the natural pyrethrum and it is also difficult and expensive to prepare.

It is therefore still desirable to produce synthetic pyrethroids having, in addition to high insecticidal activity, rapid knock-down effect and lack of mammalian toxicity, a higher stability and good weather resistance.

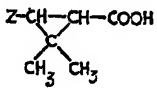
The present invention comprises substituted furans of the general formula I



I

in which Z represents an aryl, alkenyl or carboalkoxyalkenyl group, Y represents a hydrogen atom or an alkyl, alkenyl or alkadienyl group, or an aryl group or a furyl group which themselves may be substituted in the ring by alkyl, alkenyl, alkadienyl or alkoxy groups or halogen atoms, and R_1 and R_2 which may be the same or different, each represent a hydrogen atom or an alkyl, alkenyl or alkadienyl group.

It will be seen that the compounds of the invention are esters of substituted cyclopropane carboxylic acids of the general formula II



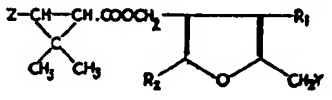
II

Acids in which Z represents an isobutenyl group or a 2 - carbomethoxy - prop - 1 - enyl group, i.e. chrysanthemic acid or pyrethric

acid, have been found to produce particularly active esters. Acids of the Formula II can exhibit optical and geometrical isomerism, the various isomers producing esters of varying insecticidal activity. Thus in the case of chrysanthemic and pyrethric acids it is found that the (+)-*trans* acids, obtained from natural pyrethrum produce more active compounds than their synthetic counterparts, the (±)-*cis-trans* isomers, which nevertheless still produce valuable insecticides.

Other useful insecticides of the Formula I may be obtained from 2,2 - dimethyl - cyclopropane carboxylic acid substituted in the 3 position by other alkenyl groups or by aryl groups, for example, a phenyl group.

The compounds of the invention are essentially substituted furylmethyl esters containing from 1 to 3 further substituents in the furan ring. It is preferred that the furan ring contains one or two such further substituents and in such compounds preferably R_1 represents hydrogen and R_2 represents hydrogen or a C_1 to C_4 alkyl group. In general it is found that compounds in which the furan ring is linked to the ester group through the 3 position i.e. a 3-furyl-methyl compound, have a greater insecticidal activity than the corresponding compounds in which the ring is linked through the 2 position i.e. 2 - furyl - methyl or so-called "furfuryl" compounds. In 3 - furyl - methyl compounds it is often found that high insecticidal activity is associated with a substituent being present in the 5 position on the furan ring. A C_1 to C_4 alkyl substituent in the 2 position, e.g. a methyl group, sometimes enhances the activity of the 3-furylmethyl esters. Thus a preferred group of esters are those of Formula Ia



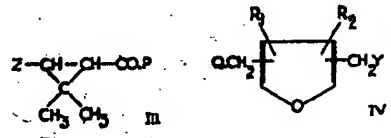
Ia

and in such compounds Y preferably represents a benzenoid ring system, for example, a phenyl group so that CH_2Y represents a benzyl group. Such benzenoid ring systems may be further ring substituted e.g. by alkyl or alkoxy groups containing up to 4 carbon atoms e.g. methyl or methoxy groups or by chlorine atoms. Other active compounds are obtained when Y represents a hydrogen atom, an alkyl group containing up to 4 carbon atoms, an alkenyl group containing up to 4 carbon atoms, e.g. vinyl, as in the 5-allyl 3-furylmethyl or 2-furylmethyl esters, an alkadienyl group containing up to 4 carbon atoms or a furyl group. When Y represents hydrogen or a C_1—C_4 alkyl or alkenyl group R_1 and R_2 preferably represent hydrogen or a C_1—C_4 alkyl group.

The insecticidal activity of the esters often tends to decrease as the degree of substitution in the furan ring linked with the ester group increases except when the substituent is methyl. Apart from this exception mono-substituted furfuryl esters tend to be more active than the corresponding poly substituted furfuryl esters but the reduction in activity is often only slight and may be accompanied by more desirable physical properties. Where such further substituents are present they may contain up to 4 carbon atoms.

The preferred esters of this invention have been derived from chrysanthemic and pyrethric acids and 5 - benzyl - furfuryl alcohol, 5 - benzyl - 3 - furyl methyl alcohol, 5 - benzyl - 2 - methyl - 3 - furyl methyl alcohol, 5 - methyl - 4 - benzyl - furfuryl alcohol, 5 - p - xylyl - furfuryl alcohol, 2,4,5 - trimethyl - 3 - furyl methyl alcohol and 4,5-dimethyl-furfuryl alcohol.

The compounds of the invention may be prepared by any of the methods customarily used for the preparation of esters and the reactants may be represented generally by the formulae III and IV



III IV

where CO.P and Q represent functional groups which react together to give an ester linkage.

Thus esters may be prepared by reacting a furyl-methyl alcohol with the substituted cyclopropane carboxylic acid or acid anhydride or more preferably, with its acid halide, for example by treating the reactants in a solvent in the presence of a hydrogen halide acceptor such as pyridine.

A useful alternative method involves the treatment of a furyl-methyl halide with a silver salt of the substituted cyclo-propane carboxylic acid; in this method a rather purer product is obtained and the silver is recoverable for further use. This method may be modified to avoid the need for a silver salt by reacting the furyl-methyl halide with a triethylamine salt of the desired acid. This salt may be prepared *in situ* by reacting equimolar quantities of the acid and triethylamine.

The esters of the invention may also be prepared by a transesterification process using for example a lower alkyl ester of the substituted cyclo-propane carboxylic acid (containing 1 to 4 carbon atoms in the lower alkyl group) and a furylmethyl alcohol. This transesterification may be carried out in the presence of an alkali metal such as sodium or alkali metal alkoxide such as sodium ethoxide.

Certain of the 5-substituted 3-furylmethyl

alcohols used to prepare the esters of this invention are themselves new compounds. The new alcohols and processes for their preparation are described and claimed in copending applications 37787/66 and 37788/66 (Serial No. 1168798).

One or more of the insecticidal esters of the invention may be formulated with an inert carrier or diluent to give insecticidal compositions and they may be prepared for example, in the form of dusts and granular solids, mosquito coils, wettable powders, emulsions, sprays and aerosols after addition of appropriate solvents, diluents and surfactants.

In common with pyrethrum and synthetic pyrethroids the compounds of the invention may be synergised, for example, with piperonyl butoxide or with other well known pyrethrum synergists.

The insecticidal compositions described above may be used for killing insects on a domestic or agricultural scale by treating the insects themselves where insect infestation has already taken place or by treating an environment susceptible to insect attack with the composition as a preventive measure. The following examples are given to illustrate the present invention. Temperatures are in °C.

EXAMPLE 1

Esterification of the alcohol

5 - Benzyl - 3 - furylmethyl alcohol (1.1 mol.prop.) as a 10% w/v solution in ether is added with cooling and stirring to (±)-*cis-trans* chrysanthemoyl chloride (1.0 mol.prop.) as a 10% w/v solution in benzene. Pyridine (1.0 mol.prop.) is added and the mixture set aside overnight. Water is then added to the organic layer, which is washed with dilute sulphuric acid, with saturated aqueous potassium hydrogen carbonate and twice with saturated sodium chloride and is finally dried, evaporated and distilled to give 5 - benzyl - 3 - furylmethyl - (±) - *cis* - *trans* - chrysanthemate, b.p. 169—172°/2.5 × 10^{-2}mm., n_D^{20} 1.5305. 5 - Benzyl - 3 - furylmethyl (+) *trans* chrysanthemate, b.p. 174°/8 × 10^{-1}mm., n_D^{20} 1.5346; (±) - *trans* - chrysanthemate, m.p. 54—55° and (+) - *trans* - pyrethrate, b.p. 206°/8 × 10^{-3}mm. are similarly prepared using the appropriate isomer of chrysanthemoyl or pyrethroyl chloride.

EXAMPLE 2

The following esters are similarly prepared by esterifying the corresponding alcohol by the general procedure described in Example 1 above.

(±)-*cis-trans*-chrysanthemates:

3-Methylfurfuryl, b.p. 101—105°/10^{-2}mm., n_D^{20} 1.4944

2-Methyl-3-furylmethyl, b.p. 110°/10^{-2}mm., n_D^{20} 1.4942

5-Methyl-furfuryl, b.p. 97—101°/8×10^{-3}mm., n_D^{20} 1.4923

5-Methyl-3-furylmethyl, b.p. 103°/5×10^{-3}mm., n_D^{20} 1.4913

2,5-Dimethyl-3-furylmethyl, b.p. 109—111°/6×10^{-3}mm., n_D^{20} 1.4917

4,5-Dimethyl-furfuryl, b.p. 120—126°/7×10^{-2}mm., n_D^{20} 1.4962

3,5-Dimethyl-furfuryl, b.p. 108—109°/5×10^{-2}mm., n_D^{20} 1.4950

5-Benzyl-furfuryl, b.p. 161—162.5°/1.6×10^{-2}mm., n_D^{20} 1.5342

5-p-Xylyl-furfuryl, b.p. 150.5—5151.5°/10^{-2}mm., n_D^{20} 1.5320

5-Benzyl-2-methyl-3-furylmethyl, b.p. 179°/7×10^{-3}mm., n_D^{20} 1.5305

4-Benzyl-5-methyl-furfuryl, b.p. 170—172°/2.3×10^{-2}mm., n_D^{20} 1.5340

2,4,5-Trimethyl-3-furylmethyl, b.p. 116—118°/3×10^{-3}mm.,

5-Benzyl-3-methylfurfuryl, b.p. 160°/1×10^{-2}mm., n_D^{20} 1.5280

Transesterification of 5 - Benzyl - 3 - furylmethyl Alcohol and Ethyl Chrysanthemate

EXAMPLE 3

Sodium (0.1 g.) is added in 5 portions over a period of three hours to a mixture of 5 - benzyl - 3 - furylmethyl alcohol (4.5 g.), ethyl chrysanthemate (4.7 g.) and toluene refluxed in the dark in nitrogen. When reaction is complete, ether is added, the product shaken with water, dried and then evaporated and distilled. After removing some ethyl chrysanthemate and

unchanged alcohol, 5 - benzyl - 3 - furylmethyl chrysanthemate (3.7 g.) is obtained b.p. 165—175°/8 × 10^{-3}mm., n_D^{20} 1.5316 which is identical by NMR spectrum with material obtained according to Example 1 using the acid chloride and which crystallises on seeding with an authentic sample.

EXAMPLE 4

Sodium (0.15 g.) is added to a mixture of toluene (50 ml.) and ethanol (5 ml.) refluxed in the dark in nitrogen. When no sodium remains undissolved, excess alcohol is distilled off, the product cooled and then 5 - benzyl - 3 - furylmethyl alcohol (5.26 g.) and ethyl chrysanthemate (5.48 g.) in toluene (15 ml.) added. The mixture is refluxed for 45 min., with co-distillation of the ethanol evolved with toluene, then cooled and ether added. The product is washed with water, dried (Na_2SO_4) evaporated and distilled to give ethyl chrysanthemate b.p. 60—120°/3 × 10^{-3}mm., (0.3 g.) n_D^{20} 1.4916, 5 - benzyl - 3 - furylmethyl alcohol b.p. 120—170°/2 × 10^{-3}mm., (1.1 g.) n_D^{20} 1.5340—1.5380, and 5 - benzyl - 3 - furylmethyl chrysanthemate b.p. 170—185°/2 × 10^{-3}mm., n_D^{20} 1.5305; 6.05 g., equivalent to a yield of 80% based on unrecovered alcohol. Insecticidal compositions are prepared containing esters of the general Formula I having components in the following proportions:—

EXAMPLE 5—OIL-BASED LIQUID SPRAY FOR HOUSEHOLD INSECTS

5-benzyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	0.005% w/v
25% Pyrethrum Extract	0.25%
Piperonyl butoxide	0.5%
Antioxidant, e.g. "Topanol A."	0.1%
Odourless light oil solvent, e.g. xylene to make	100 vols.

(Topanol is a Registered Trade Mark)

EXAMPLE 6—WATER-BASED LIQUID SPRAY CONCENTRATE FOR MOSQUITO CONTROL

5-benzyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	0.25% w/v
Piperonyl butoxide	1.0%
Non-ionic emulsifier, e.g. "Ethylan BCP"	0.25%
Antioxidant, e.g. "Topanol A."	0.1%
Water to make	100 vols.

This concentrate should be diluted 1:80 v/v with water before spraying.
(Ethylon is a Registered Trade Mark)

EXAMPLE 7—AEROSOL

5-benzyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	0.02% w/w
25% Pyrethrum Extract	0.8%
Piperonyl butoxide	1.5%
Odourless petroleum distillate (b.p. 200—265°)	17.338%
Propellant, e.g. a mixture of equal quantities of trichloromonofluoromethane & dichlorodifluoromethane	80.0%
Perfume	0.2%
Antioxidant, e.g. Topanol A.	

EXAMPLE 8—MOSQUITO COIL

5-benzyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	0.25% w/w
Tabu powder or Staragel No.1	30.0%
Filler(s), e.g. wood flour, powdered leaves or nut shells	68.75%
Brillant Green	0.5%
p-Nitrophenol	0.5%

EXAMPLE 9—EMULSIFIABLE CONCENTRATE

5-benzyl-3-furylmethyl-(±)-*cis-trans*-chrysanthemate	1.5% w/w
Non-ionic emulsifier, e.g. "Ethylan BCP"	25.0%
Xylene	73.4%
Antioxidant, e.g. "Topanol A."	0.1%

This concentrate may then be diluted at the rate of 30 mls. to 4½ litres of water prior to use.

EXAMPLE 10—GENERAL PURPOSE POWDER FOR HOUSEHOLD, GARDEN, LIVESTOCK OR GRAIN STORAGE USE.

5-benzyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	0.05% w/w
Tropital	0.25%
Antioxidant, e.g. butyl hydroxy toluene or butyl hydroxy anisole	0.03%
Filler, e.g. Talc BPC	99.67%

In the compositions described in Examples 5—10 the active component 5 - benzyl - 3 - Furylmethyl (±) - *cis* - *trans* - chrysanthemate may be replaced completely or in part by an equivalent amount of any of the other esters of the general formula I, for example by 5 - benzyl - 3 - furylmethyl(+) - trans - pyrethrate which has a particularly good knock-down effect on house-flies and such other compounds can advantageously be included in the compositions above as can other known insecticides which are compatible with the pyrethroids of formula I.

Insecticidal Activity

In contact toxicity tests in which insects were treated with measured drops of the insecticides dissolved in acetone, against house flies (adult female *Musca domestica* L.), 5 - benzyl - 3 - furylmethyl(±) - *cis* - *trans* - chrysanthemate was more than twenty times as toxic as the mixture of natural pyrethrins and nearly five times more toxic than the most toxic pyrethrin-like ester previously known, 4 - allyl - 2,6 - dimethylbenzyl (+) - *cis* - *trans* chrysanthemate. It was more than ten times more toxic than allethrin to house flies. By a similar method of testing, to mustard beetles (adult *Phaedon cochlearae* Fab.,)5 - benzyl - 3 - furylmethyl (±) - *cis* - *trans* - chrysanthemate was twice as toxic as the mixture of natural pyrethrins, sixteen times more toxic than 4 - allyl - 2,6 - dimethylbenzyl (±) - *cis* - *trans* - chrysanthemate and thirty-two times more toxic than allethrin. Although 5 - benzyl - 2 - methyl - 3 - furyl (±) - *cis* - *trans* - chrysanthemate was one half to one third as toxic as the unmethylated 3-furyl

ester, it still has a most useful level of insecticidal activity.

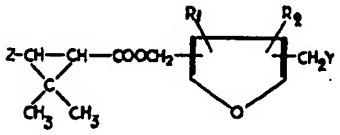
Toxicities relative to natural pyrethrin and certain synthetic pyrethroids and other insecticides are shown below:—

TOXICITY TABLE

No.	Compound	Toxicity relative to Allethrin = 100	
		Mustard Beetles	House Flies
1.	5-benzyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	3200	2000
2.	5-benzyl-3-furylmethyl (+)-*trans*-chrysanthemate	8400	5000
3.	5-benzyl-3-furylmethyl (±)-*trans*-chrysanthemate	4800	2600
4.	5-benzyl-3-furylmethyl (+)-*trans*-pyrethrate	5200	500
5.	5-benzyl-furfuryl (±)-*cis-trans*-chrysanthemate	150	220
6.	5-benzyl-2-methyl-3-furylmethyl (±)-*cis-trans*-chrysanthemate	1300	920
	Known Insecticides		
7.	Natural Pyrethrins	1600	92
8.	Pyrethrin I	3900	92
9.	Pyrethrin II	1300	140

WHAT WE CLAIM IS:—

1. Substituted furans of the general formula

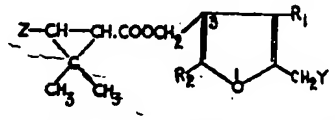


in which Z represents an aryl, alkenyl or carbalkoxyalkenyl group, R_1 and R_2, which may be the same or different, represent a hydrogen atom or an alkyl, alkenyl or alkadienyl group, and Y represents a hydrogen atom or an alkyl, alkenyl or alkadienyl group or an aryl or furyl group which may be substituted in the ring by alkyl, alkenyl, alkadienyl or alkoxy groups or halogen atoms.

2. Compounds according to claim 1, in which the substituent containing Z is attached to the furan ring at the 3-position.

3. Compounds according to claim 1, in which the substituent containing Z is attached to the furan ring at the 2-position.

4. Compounds of general formula



where Z, R_1, R_2 and Y are as defined in claim 1.

5. Compounds according to any of claims 1 to 4, in which Y represents a benzenoid group.

6. Compounds according to claim 5, in which Y represents phenyl, methylphenyl, methoxyphenyl, or chlorophenyl.

7. Compounds according to any of claims 1 to 4, in which Y represents hydrogen or an alkyl or alkenyl group containing up to 4 carbon atoms.

8. Compounds according to any of the preceding claims, in which R_1 and R_2 represent hydrogen or an alkyl group containing up to 4 carbon atoms.

9. Compounds according to any of the preceding claims in which Z represents isobutenyl, 2 - carbomethoxy - prop - 1 - enyl or phenyl.

10. Compounds according to claim 9, which

are esters of (±) - *cis* - *trans* - chrysanthemic acid, (+) - *trans* - chrysanthemic acid, (±) - *trans* chrysanthemic acid or (+) - *trans* - pyrethric acid.

11. Compounds according to claim 4, in which the group CH_2Y represents 5-allyl.

12. 5 - Benzyl - 3 - furylmethyl (±) - *cis* - *trans* - chrysanthemate.

13. 5 - Benzyl - 3 - furylmethyl (+) - *trans* - chrysanthemate.

14. 5 - Benzyl - 3 - furylmethyl (±) - *trans* - chrysanthemate.

15. 5 - Benzyl - 3 - furylmethyl (+) - *trans* - pyrethrate.

16. 3 - Methyl - furfuryl (±) - *cis* - *trans* - chrysanthemate.

17. 2 - Methyl - 3 - furylmethyl (±) - *cis* - *trans* - chrysanthemate.

18. 5 - Methyl - furfuryl (±) - *cis* - *trans* - chrysanthemate.

19. 5 - Methyl - 3 - furylmethyl (±) - *cis* - *trans* - chrysanthemate.

20. 2,5 - Dimethyl - 3 - furylmethyl (±) - *cis* - *trans* - chrysanthemate.

21. 4,5 - Dimethyl - furfuryl (±) - *cis* - *trans* - chrysanthemate.

22. 3,5 - Dimethyl - furfuryl (±) - *cis* - *trans* - chrysanthemate.

23. 5 - Benzyl - furfuryl - (±) - *cis* - *trans* - chrysanthemate.

24. 5 - p - Xylyl - furfuryl - (±) - *cis* - *trans* - chrysanthemate.

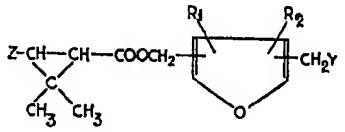
25. 5 - Benzyl - 2 - methyl - 3 - furylmethyl - (±) - *cis* - *trans* - chrysanthemate.

26. 4 - Benzyl - 5 - methyl - furfuryl - (±) - *cis* - *trans* - chrysanthemate.

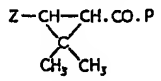
27. 2,4,5 - Trimethyl - 3 - furylmethyl - (±) - *cis* - *trans* - chrysanthemate.

28. 5 - Benzyl - 3 - methylfurfuryl (±) - *cis* - *trans* - chrysanthemate.

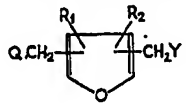
29. A process for the preparation of substituted furans of the general formula



in which Z represents an aryl, alkenyl or carboalkoxyalkenyl group, R_1 and R_2, which may be the same or different, represent a hydrogen atom or an alkyl, alkenyl or alkadienyl group and Y represents a hydrogen atom or an alkyl, alkenyl or alkadienyl group or an aryl or furyl group which may be substituted in the ring by alkyl, alkenyl, alkadienyl or alkoxy groups or halogen atoms, which comprises reacting a substituted cyclopropane carboxylic acid or acid derivative thereof of the general formula



with a substituted furan of the general formula



where —CO.P and Q represent functional groups which react together to form an ester linkage.

30. A process according to claim 29, in which —CO.P represents a carboxylic acid or carboxylic acid anhydride or carboxylic acid halide group and Q represents a hydroxy group.

31. A process according to claim 30, for the preparation of 5 - Benzyl - 3 - furylmethyl chrysanthemate in which chrysanthemoyl chloride is reacted with 5 - benzyl - 3 - furylmethyl alcohol in the presence of a hydrogen chloride acceptor.

32. A process according to claim 29, in which —CO.P represents a carboxylic acid silver or trialkylamine salt group and Q represents a halogen atom.

33. A process according to claim 29, in which —CO.P represents a carboxylic acid lower alkyl ester group containing 1 to 4 carbon atoms in the lower alkyl group and Q represents a hydroxy group.

34. A process according to claim 33, in which the transesterification is carried out in the presence of an alkali metal or an alkali metal alkoxide.

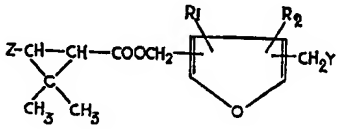
35. A process according to claim 33, for the preparation of 5 - benzyl - 3 - furylmethyl chrysanthemate or pyrethrate in which ethyl chrysanthemate or pyrethrate is reacted with 5 - benzyl - 3 - furylmethyl alcohol in the presence of sodium or a sodium alkoxide.

36. A process for preparing a compound according to claim 1, substantially as described in Example 1 or 2.

37. A process for preparing a compound according to claim 1, substantially as described in Example 3 or 4.

38. Compounds according to claim 1 whenever prepared by a process according to any of claims 29 to 37.

39. An insecticidal composition comprising as an active ingredient a substituted furan of the general formula



in which Z represents an aryl, alkenyl or carboalkoxyalkenyl group, R_1 and R_2, which may be the same or different, represent a hydrogen atom or an alkyl, alkenyl or alkadienyl group, and Y represents a hydrogen atom or an alkyl, alkenyl or alkadienyl group or an aryl or furyl group which may be substituted in the ring by alkyl, alkenyl, alkadienyl or alkoxy groups or halogen atoms, together with an inert diluent or carrier.

40. An insecticidal composition according to claim 39, in which the active ingredient is a chrysanthemate or pyrethrate of 5 - benzyl - 3 - furylmethyl alcohol or 5 - benzyl - 2 - methyl - 3 - furylmethyl alcohol.

41. An insecticidal composition, substantially as described in any of Examples 5 to 10.

42. A method of insect control which comprises treating in environment susceptible to insect attack with an insecticidal composition according to claim 39, 40 or 41.

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